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Effects of reactor type and mass transfer on the morphology of CuS and ZnS crystals

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For the precipitation of CuS and ZnS, the effects of the reactor/precipitator type, mass transfer and process conditions on crystal morphology were studied. Either H₂S gas or a S²⁻ solution were applied. Three different types of reactors have been tested, namely a laminar jet, a bubble column and an MSMPR reactor. The choice of reactor type as well as mass transfer and metal concentration all have a considerable influence on the morphology of the produced crystals. A well mixed bubble column with H₂S containing gas as feed yields the coarsest crystals. Use is then made of the surface active properties of CuS-particles, which induce agglomeration at the gas-liquid interface, where as the low metal concentrations inside the reactor also contribute to the formation of coarser particles (especially for ZnS).

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1 Introduction

Many specialty chemicals are manufactured in crystalline form through precipitation processes. The majority of such industrial processes involve simultaneous chemical reaction and crystallization or precipitation. A variety of gas-liquid and liquid-liquid processes can result in the production of different crystalline products, but studies on the interactions between process conditions and reactor layout on the one hand and crystal morphology on the other are scarce in literature. In precipitation the generation of supersaturation conditions with respect to the desired crystallizing product results as a consequence of chemical reaction. Reaction kinetics should therefore be known to characterize the performance of a reactive crystallizer. In many occasions, solution chemistry may be equally complex, and simplification may be necessary to describe the physicochemical processes in a system. In simple cases, reaction kinetics may be assumed to be first order with respect to each of the reactants and both solubility and solvent capacity may be regarded constant throughout a crystallizer. In many other cases, however, more complex physicochemistry is needed to describe the process adequately. In any case, a good understanding of the interaction between the different processes that are involved is needed to identify the improvements that may be achieved in crystal quality and the cost effectiveness of crystal production.

In recent years, more studies on reactive crystallization have been reported in literature, but not many on precipitation accompanied by a gas-liquid reaction, although this is frequently encountered in chemical industry. These three phase systems have a complex nature and not much is known about the interactions between process conditions and crystal quality [1].

The objectives of a crystallization process are to meet product specifications: (a) a narrow crystal size distribution, (b) maximum crystal purity, (c) a high yield and (d) acceptable crystal morphology. Depending on product applications, one of these can be more critical than the others. The optimum conditions to obtain crystals that meet such specifications are often determined in an empirical way, either by controlled growth through proper adjustment of supersaturation or by addition of certain habit modifiers. It is extremely difficult to predict crystal properties like lattice, morphology, hardness, strength, ductility, etc. on the basis of a fundamental approach. Parameters that are important are [2]:

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1. Properties of the solution (density, viscosity, supersaturation, ionic strength, pH, etc.);
2. Operation mode and conditions (pressure, temperature, specific power input, residence time distribution, feed ratio of reactants, feed point location(s), etc.).

The best combination of these parameters should be determined in practice or on lab-scale. The intrinsic processes that determine the shape of crystals are:

1. The different growth rates of the different crystal faces;
2. Possible blockage of growth of certain faces due to the adsorption of impurities/additives;
3. Agglomeration of crystals;
4. Abrasion and attrition of crystals or agglomerates;
5. Breakage of crystals.

In most cases crystal morphology and crystal purity are interrelated. For some applications, e.g. in optics or medical ones crystal morphology is of upmost important. But morphology can also be important from a more fundamental viewpoint as it can give indications with regard to growth mechanism (surface integration, spiral growth), crystal purity and the rate determining step in gas-liquid precipitation.

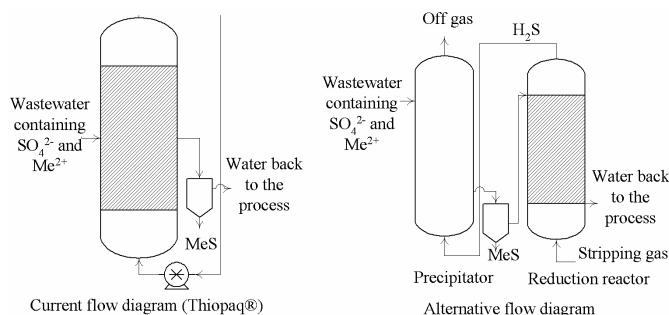


Fig. 1 Possible process flow diagrams.

Previous work Chen et al. [3] studied the polymorphism of calcium carbonate crystals by introducing CO₂ gas through a gas sparger or a double-tube gas injection nozzle into a pH-stat crystallizer containing calcium chloride solution. They investigated the effects of several variables such as supersaturation and pH. They found that at ambient temperature either calcite or vaterite is the major product, depending on the applied conditions. They also studied the growth kinetics of calcite crystals using the same experimental setup. They found that the growth rates of calcite seeds increased with increasing supersaturation and crystal size. They concluded that the morphology and growth rate of calcium carbonate are controllable in a gas-liquid-solid reactive crystallizer, using a pH-stat operation mode.

Bredol and Merikhi [4] investigated the morphology of ZnS particles used in cathode-ray tube luminescent materials. They studied the effect of different preparation methods (homogeneous precipitation and precipitation in the liquid crystal phase) and the introduction of ZnS seeds on morphology. They used powders produced by different processes to prepare luminescent materials in a standard manner. Their results show the effects of raw ZnS powder properties (including morphology) on the performance of annealed phosphor powders.

Yukiya et al. [5] studied the relationship between the morphology of alumina hydroxide particles and the concentrations of the precipitating species. They developed a model which is based on minimization of the Gibbs energy regarding temperature, solvent effects and ion-ion interactions. They calculated the solvent effect by use of the Born equation. The effect of ion-ion interaction was calculated by the extended Debye-Huckel equation. They found that particle morphology is mainly determined by selective adsorption of positive charged Al(OH)²⁺ ions on the negatively charged faces of the AlOOH crystals.

Wang et al. [6] investigated the morphology of calcium carbonate particles produced by CO₂-Ca(OH)₂ precipitation in a Couette-Taylor reactor. They found that particle morphology is dominated by the excess concentration of reactants in the solution. They found that the largest mean particle size and the most cube-like particle shape are obtained at the stoichiometric reaction conditions. As stoichiometry starts to deviate from unity, particle morphology shifts to a spindle-like shape and the mean particle size decreases. They predicted these effects by making use of the Bliznakov equation which is based on mono-layer adsorption.

Chen et al. [7] used a double-jet feed, semi-batch crystallization system to explore nucleation kinetics, growth kinetics and morphology of barium carbonate crystals. They determined nucleation and growth rates by the initial rate method. Their results show that heterogeneous nucleation is dominant in primary nucleation, the

effect of specific power input on the rate of nucleation being significant. They also found that pH and initial concentration affect the morphology of the produced barium carbonate crystals. They produced crystals that are floc-like, candy-like, olivary-like and needle-like at different operating conditions. At moderate to high supersaturation floc-like precipitates are dominant in the pH range of 9.0–10.0. At low to moderate supersaturation, candy-like and olivary-like crystals become the major products. At low supersaturation and low pH values olivary-like and needle-like crystals are formed.

Sung et al. [8] investigated the effects of Taylor vortices on the mean size, size distribution, and morphology of calcium carbonate crystals formed by the reaction of CO_2 and aqueous calcium hydroxide in a Couette–Taylor reactor. They measured the mass transfer coefficient of CO_2 into pure water at various rotating speeds of the inner cylinders in the Couette–Taylor reactor. They observed that calcium carbonate crystals changed in morphology (polymorphs of rhombohedral-, spindle or needle-shaped) by changing the reactant concentrations, flow rate and/or rotating speed of the inner cylinder. They introduced a dimensionless parameter representing the operating conditions, to demonstrate that the morphology of the calcium carbonate crystals can be predicted from operating conditions. They concluded that the mean crystal size (predominantly controlled by agglomeration) is mostly influenced by the fluid dynamic conditions which are related to the rotating speed of the inner cylinder and the reactor geometry.

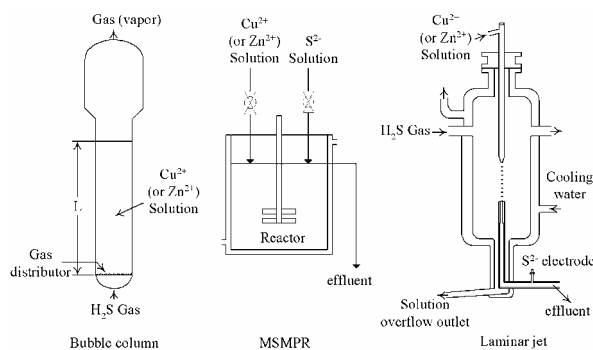


Fig. 2 Schematic diagrams of the applied experimental setups.

Table 1 Main characteristics of the applied experimental setups.

Characteristics	Bubble column	Laminar jet	MSMPR
Phases	Gas-liquid	Gas-Liquid	Liquid-Liquid
Crystal residence time	20–50 s	0.03–0.07 s	150–300 s
Tested Me^{2+} concentrations	2000–6000 ppm	200–600 ppm	2000–4000 ppm
Liquid volume	1500 ml	0.04 ml	1000 ml
Mixing Gas, Liquid	plug flow, well mixed	Well mixed, No mixing	Well mixed, No gas
Flow	Batch liquid, Continuous gas	Continuous gas, Continuous liquid	Continuous liquid
Key variables	Superficial gas velocity	Liquid flow rate	Mixer speed

This work This work is part of a large study into the precipitation of heavy metal ions (mainly Cu^{2+} and Zn^{2+}) present in wastewater from the Pasminco zinc factory in Budel the Netherlands. Use is made of the Paques Thiopaq® process, which involves biological reduction of sulfate, which is also present in the wastewater, towards sulfide. The sulfide subsequently reacts with the metal ions to form metal sulfides that can be removed by use of a settler or a centrifuge. To enable sufficient removal of the metal sulfides, coarse particles are to be produced ($>10\ \mu\text{m}$). In this work it is examined how reactor layout and process conditions affect the size of the produced particles

Besides direct precipitation where sulfide ions are formed in the metal ions containing water, one might also consider a different process layout in which biological sulfate reduction reaction and metal sulfide precipitation are carried out in different reactors. The sulfide ions formed in the biological reduction reactor are in that case stripped off as H_2S gas and is then led to the precipitator, which is placed in front of the reduction reactor. See Figure 1.

One may expect that particle morphology will become different when applying this process instead of the standard Thiopaq® process. Therefore, in this work the effects of reactor type, reactor configuration process conditions and liquid side mass transfer on the crystal morphology of CuS and ZnS were investigated. An MSMPR reactor, a bubble column and a laminar jet reactor were used to study these effects.

2 Experimental

An MSMR reactor, a bubble column and a laminar jet reactor were used to study the effects of reactor layout and operating conditions on the morphology of the produced solids. Figure 2 shows a schematic diagram for the used experimental setups. In the MSMR reactor the Cu^{2+} (or Zn^{2+}) and S^{2-} were introduced in aqueous solutions. In the bubble column and the laminar jet reactor, an aqueous solution that contains the Cu^{2+} or Zn^{2+} ions was contacted with H_2S gas. Detailed descriptions of the applied experimental setups and the experimental procedures can be found in [9], [10] and [11]. Table 1 shows the main characteristics of each reactor.

Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) were used to investigate the morphology of the produced solids.

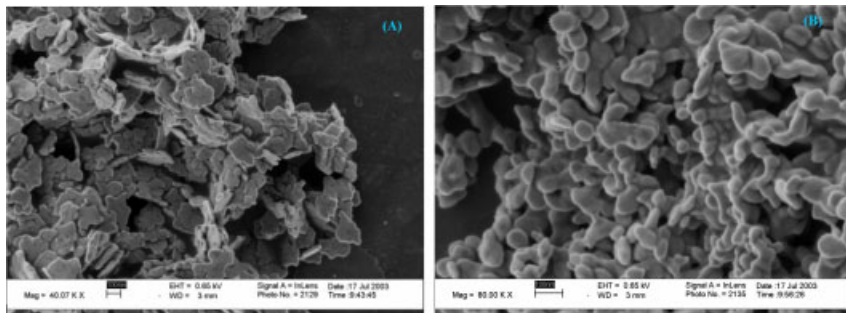


Fig. 3 Effect of liquid side mass transfer coefficient (k_L) on the morphology of CuS particles produced in a laminar jet reactor according to SEM.

Conditions: liquid flowrate 0.24 ml/s, $P = 1.025$ bar, $T = 21.6$ °C, inlet H_2S gas conc. = 99.6 vol%, $[\text{Cu}^{2+}]_{\text{feed}} = 100$ ppm, (A) $k_L = 3.85 \times 10^{-4}$ m/s, (B) $k_L = 2.4 \times 10^{-4}$ m/s.

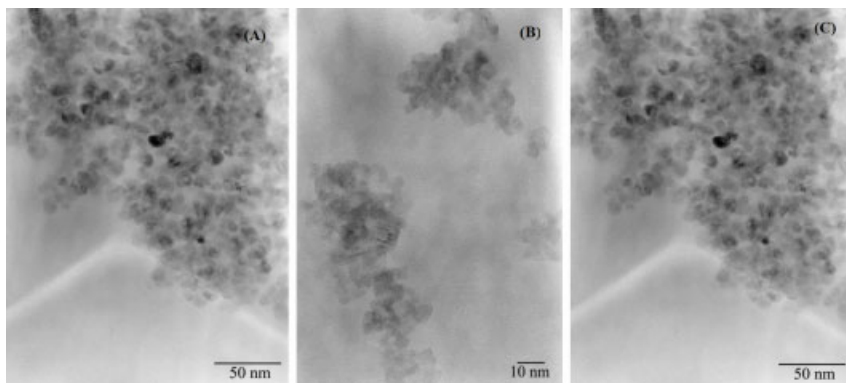


Fig. 4 Effect of Zn^{2+} concentration on the morphology of ZnS particles produced in the laminar jet reactor according to TEM.

Conditions: liquid flowrate 0.24 ml/s, $P = 1.025$ bar, $T = 21.6$ °C, inlet H_2S gas concentration = 99.6 vol%, $k_L = 3.94 \times 10^{-4}$, $[\text{Zn}^{2+}]_{\text{feed}} =$ (A) 97.3 ppm, (B) 253 ppm, (C) 666 ppm.

3 Results and discussion

To demonstrate the effects of reactor geometry and operating conditions on crystal morphology, several experiments in different types of reactors have been carried out. Typical results are shown by Figures 3 to 8.

Figure 3 shows the influence of the liquid side mass transfer coefficient on the morphology of CuS crystals produced in the laminar jet reactor. In this reactor agglomeration can be minimized possible influences of mechanical mixing devices and shear flow can be avoided. Decreasing the liquid side mass transfer coefficient by 38% already leads to a dramatic change in morphology as can be seen in Figure 3. Particles produced at $k_L = 3.85 \times 10^{-4}$ m/s (A) seem to be flat plates while the particles produced at $k_L = 2.4 \times 10^{-4}$ m/s (B) are spherical. In case A the amount of absorbed H_2S is higher, which may reduce the local pH. It is known [3] that the pH is of utmost importance in this respect. Another explanation may be that in case A mass transfer was not fully rate determining while it was in case B. In literature several studies have been reported that demonstrate the influence of mass transfer on crystal morphology [6, 8].

Figures 4 and 5 show the effect of Zn^{2+} concentration on the size and morphology of ZnS crystals, also produced in the laminar jet reactor. As it can be seen, increasing the metal concentration in this case only has a small influence on crystal size and crystal morphology. The ZnS crystals seem spherical in all cases. This can be due to the domination of nucleation at the tested conditions since the contact time between liquid and gas was very short (0.03 sec). The size of the primary crystals, which can only be determined by the applied TEM method, is much smaller than the size of the aggregates observed when applying analysis methods such as X-

ray diffraction or dynamic light scattering DLS. Comparing the morphology of the produced ZnS with that of the CuS particles (Figure 3) one observes large differences: The CuS crystals can be plates-like for while spheres are observed for ZnS. Also the size of the CuS clusters are much bigger indicating their tendency to agglomerate.

Fig. 5 SEM pictures of ZnS particles produced in the laminar jet reactor.

Conditions: liquid flowrate 0.24 ml/s, $P = 1.025$ bar, $T = 21.6$ °C, inlet H_2S gas conc. = 99.6 vol%, $k_L = 3.85 \times 10^{-4}$ m/s, $[Zn^{2+}]_{feed} = 253$ ppm.

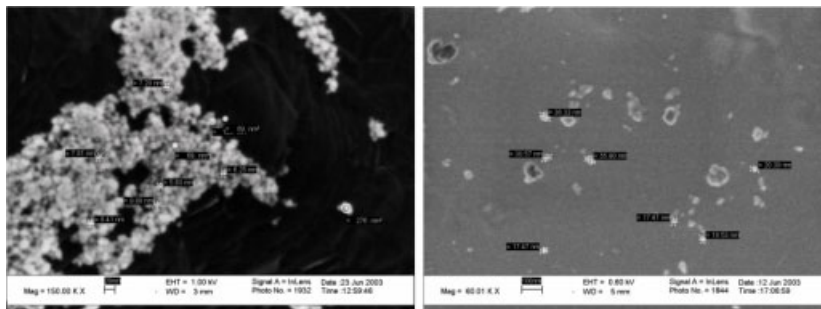


Fig. 6 Effect of initial Zn^{2+} concentration on the morphology of ZnS particles produced in a bubble column reactor according SEM.

Conditions: $P = 1.125$ bar, $T = 21.6$ °C, inlet H_2S gas conc. = 99.6 vol%, $k_L = 0.0406$ 1/s, $[Cu^{2+}]_{initial} =$ (A) 5084 ppm and (B) 6355 ppm.

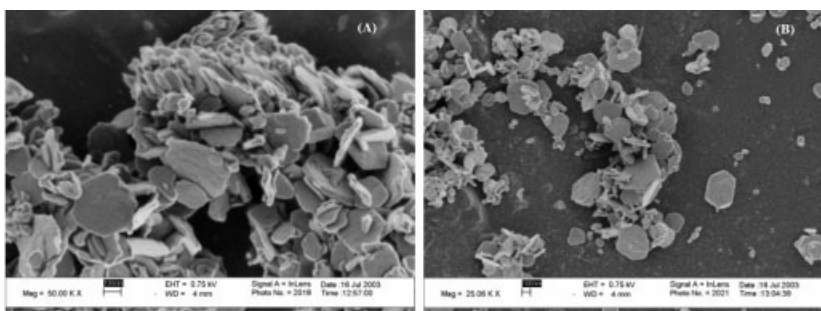


Fig. 7 Effect of initial Cu^{2+} concentration on the morphology of CuS particles produced in the bubble column reactor according SEM.

Conditions: $P = 1.125$ bar, $T = 21.6$ °C, inlet H_2S gas conc. = 99.6 vol%, $k_L = 0.0406$ 1/s, $[Cu^{2+}]_{initial} =$ (A) 6538 ppm (B) 5230 ppm.

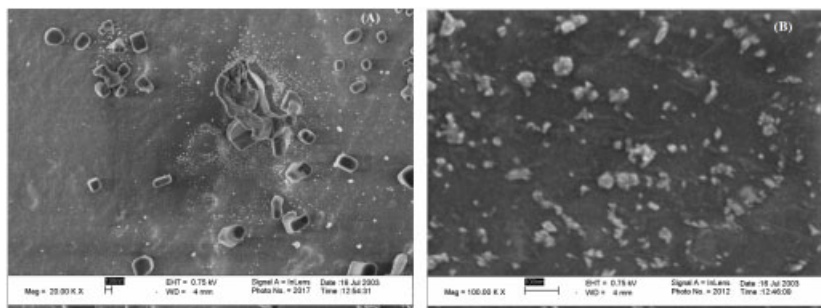


Figure 6 shows the effect of initial Zn^{2+} concentration on the crystal morphology of ZnS when a bubble column is used as precipitator. Increasing the initial concentration of Zn^{2+} by 25% resulted in a decrease in particle size of more than 50% while crystal morphology was hardly affected. The particles obtained in both cases have a plate-like shape. Figure 6 also shows that increasing the concentration yields a broader particle size distribution. When comparing the size of the particles produced in the bubble column with the ones produced in the laminar jet whereas morphology has changed from sphere like to plate like. This can be due to the much higher zinc concentrations which reduces the local pH of the produced solution and may enhance agglomeration in the bubble column [3].

Figure 7 shows the effect of initial Cu^{2+} concentration on the morphology of CuS particles produced in the bubble column precipitator. The opposite effect was observed as with zinc: increasing the initial concentration of Cu^{2+} by 25% corresponded to a 300% increase in particle size. Crystal morphology also changed, i.e. from cube like to sphere like. Particles produced at the high initial copper concentration are bigger and have a more defined cubic shape. Experimentally it was noticed that CuS particles, due to their surface active nature, tend to attach to the rising bubbles. Increasing the initial Cu^{2+} concentration leads to higher initial nucleation rates. The produced nuclei tend to block the interfacial surface area as they remain at the interface, which leads to enhancement of crystal growth, lower nucleation rates and ultimately larger particles. When comparing the particles from the bubble column with those from the laminar jet reactor, many differences are observed. First

of all the particles from the bubble column are much larger. Particles could have different morphology and can be spheres cubes or slides depending on the operating conditions in the applied precipitators.

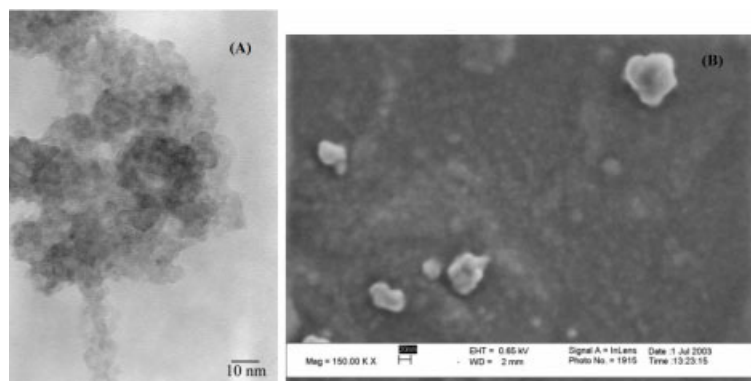


Fig. 8 Crystal morphology of ZnS particles produced in an MSMRP reactor. Conditions: RPM = 710, molar feed ratio $\text{Zn}^{2+}:\text{S}^{2-} = 1:1$, pH=5.9, residence time = 157 s, A:TEM,B: SEM.

Finally, ZnS was produced in an MSMRP crystallizer. Figure 8 shows SEM and TEM pictures of the produced particles. In this experiment S^{2-} and Zn^{2+} ions were introduced in dissolved form. As can be seen the produced crystals are spherical. In general the size of the produced particles was much smaller than that of the particles produced in the laminar jet and bubble column reactors. This can be due to the high local supersaturation values near the feeding points which enhances nucleation resulting in the production of many small particles.

4 Conclusions

Control of crystal morphology is difficult as it highly depends on reactor type and process conditions. Local supersaturation, residence time of the crystals, hydrodynamics, contacting mode and surface active properties of the crystals, all play an important role with regard to the final size and shape of the produced crystals. A small change in one of these parameters may result in large differences in crystal morphology. Laminar jet reactor offers the possibilities to study these variables independently and quantify its effect on crystal morphology and hence optimized your reactor to achieve the desired product quality.

When designing a CuS precipitator, use should be made of the surface active properties of CuS in order to make use of agglomeration yielding coarser particles. Therefore a gas-liquid reactor is to be preferred over a single liquid phase reactor as applied in the Thiopaq® process. As for ZnS precipitation, particle size appears to be independent of reactor type, though it is strongly influenced by the concentration of Zn^{2+} ions, lower concentrations resulting in coarser particles and in a narrower particle size distribution. A reactor with a well mixed liquid phase will therefore yield the coarsest ZnS particles. A bubble column therefore is also suitable to produce coarse ZnS particles.

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